ENVIRONMENTAL PROTECTION

UDC 691.42:504.2.002.237

TECHNICAL PROPERTIES OF ROOF TILES MADE OF TECHNOGENIC MATERIAL WITH PYRITE CINDER

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Translated from Steklo i Keramika, No. 4, pp. 26 – 28, April, 2006.

It is demonstrated that introducing up to 15% pyrite cinder into ceramic mixtures significantly improves the cold resistance of roof tiles; the decrease in water absorption in this case is not proportional to the increase in cold resistance. A uniform distribution of pores of size 10^{-6} – 10^{-7} m facilitates a substantial increase in cold resistance.

The mining-and-metallurgy industrial complex has a special role in Russia and in Kazakhstan, since its products are essential for their economies and make up a perceptible part of exports. At the same time, the reserves of high-grade ores for nonferrous metallurgy are decreasing in both countries and the geological conditions for mining deposits are deteriorating. The industry now frequently uses mineral resources with a low concentration of useful components. In the past 20 – 25 years the content of the main metals in the ores has decreased 1.5 – 1.6 times and the share of ores that are difficult to process has increased from 15 to 45%. At the same time, non-ferrous metallurgy producers have accumulated immense quantities of waste.

The production of ceramics is one of the most material-consuming sectors of industry; therefore, the rational utilization of fuel, minerals, and other resources is crucial for its progress. In this context, the recycling of technogenic materials in ceramics is becoming quite topical.

The contemporary production of ceramic roof tiles calls for a new approach to estimating the tile quality. The main criteria should be high density and low open porosity, which provide for increased strength and cold resistance [1]. It has been demonstrated earlier [2] that iron oxide facilitates the consolidation of such ceramic products and improves their frost resistance.

The possibility of using the argillaceous component of the gravitation tails of zircon-ilmenite ore (GZIO) and pyrite cinder in the production of roof tiles without using tradition natural feedstock was demonstrated in [1, 3 – 5] and in Kazakhstan patent No. 11827. The obtained S-shaped tiles in their physicomechanical parameters satisfy the requirements of OST 21-32–84. However, the effect of pyrite cinder on the properties of roof tiles has not been investigated.

Considering that well-sintering high-melting clay deposits are absent or limited in most regions of Kazakhstan, East Siberia, and the Volga Region, the study of the applicability of GZIO tails as argillaceous materials for ceramics can expand the available materials for this sector.

The argillaceous component of GZIO formed after disintegration and screening of the ore has the form of pulp of moisture 37 – 45%, its color varying from light yellow to pink, and its density 2.36 – 2.42 g/cm^3. The GZIO tail is actually a high-melting clay, but has a complex mineral composition including (unlike the traditional high-melting clay) more than 10 minerals and an increased content of ferrous oxide (over 5% Fe_2O_3; here and elsewhere wt.%) [6].

Compared to traditional clays, GZIO tails have a more uniform composition. Furthermore, this material is obtained without preliminary stripping or homogenization. Based on its content of particles of size below 0.001×10^{-3} m, GZIO tail is a dispersed material, has medium plasticity and medium drying sensitivity, and is high-melting (its refractoriness is 1500 – 1550°C) and highly sintering (sintering interval 120 – 150°C).

The results of physicochemical studies indicate that the argillaceous minerals in the considered tails are to a large extent represented by kaolinite. The mineral composition of GZIO tails is as follows (%): 43 – 48 kaolinite + illite, 8 – 12 hydromica + montmorillonite, 13 – 16 quartz, 18 – 20 feld-

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0361-7610/06/0304-0130

TABLE 1

Component	Weight content, %						
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	R_2O	calcination loss
Argillaceous component of GZIO tails	58.74	21.39	1.76	1.22	6.21	1.82	7.34
Pyrite cinder	28.50	7.90	2.20	1.71	54.80	2.42	–

spar, 2 calcite, 2 zircon, 3 ilmenite, 3 iron oxides, and 0.80 – 0.98 organic impurities.

Pyrite cinder is the waste generated in producing sulfuric acid, which is used as a grog component and a sintering intensifier in the production of roof tiles. The chemical composition of the components considered is listed in Table 1.

To determine the effect of pyrite cinder on the technical properties of roof tiles, we investigated ceramic mixtures whose compositions are listed in Table 2.

The tiles were made by plastic molding with moisture 20 – 22%, then dried to a residual moisture not more than 7 – 8% and fired at 1050°C. The technical parameters of the tile are given in Table 3.

One can observe a perceptible decrease in water absorption and an increase in the mechanical strength and cold resistance of roof tiles as the amount of pyrite cinder grows from 5 to 15%. This amount of cinder serves not only as a grog component, but partly as a flux at the firing temperature of 1050°C, which is also corroborated by the data in [1, 3 – 5, 7].

The effect of pyrite cinder on the technical parameters of roof tiles is shown in Table 4 and in Fig. 1. The plots are constructed on the same scale, which can be taken, for instance as the percent increment (change) in technical parameters depending on the content of cinder in the roof tiles:

$$\Delta y = \left(\frac{y(x)}{y(0)} - 1 \right) \times 100,$$

where Δy is the percent of increment (change) of the parameter y provided that the tile contains x% cinder (Table 4).

As the pyrite cinder content grows to 15%, a qualitative change occurs in the technical parameters of the tiles. This is especially evident in the growth in bending strength and cold resistance (Fig. 1). The water absorption decreases smoothly with increasing content of pyrite cinder, compared to mechanical strength and cold resistance. When the content of cinder is over 15% all parameters deteriorate.

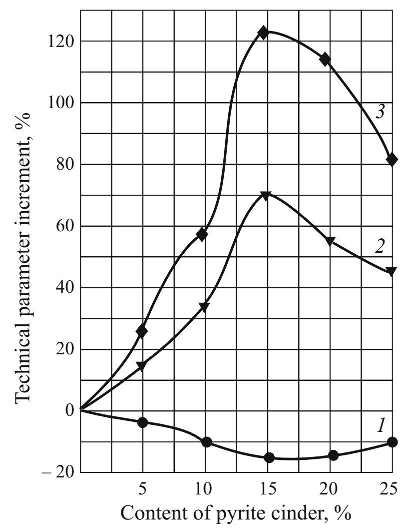

Fig. 1. Dependence of technical parameter increment on the content of pyrite cinder: *1*) water absorption; *2*) bending strength; *3*) cold resistance.

TABLE 2

Mixture	Weight content, %	
	argillaceous component of GZIO tails	pyrite cinder
1	100	–
2	95	5
3	90	10
4	85	15
5	80	20
6	75	25

TABLE 3

Parameter	Mixture					
	1	2	3	4	5	6
Water absorption, %	12.0	11.5	10.8	10.0	10.2	10.8
Bending strength, MPa	15.2	17.5	20.0	25.8	25.0	23.8
Cold resistance, cycles	35	45	55	78	75	64

TABLE 4

Ceramic mixture sample	Cinder content, %	Technical parameter increment, %		
		water absorption (%)	bending strength (MPa)	cold resistance (cycles)
1	–	0	0	0
2	5	– 4.17	15.13	28.57
3	10	– 10.00	31.58	57.14
4	15	– 16.70	69.74	122.86
5	20	– 15.00	64.47	114.28
6	25	– 10.00	56.58	82.86

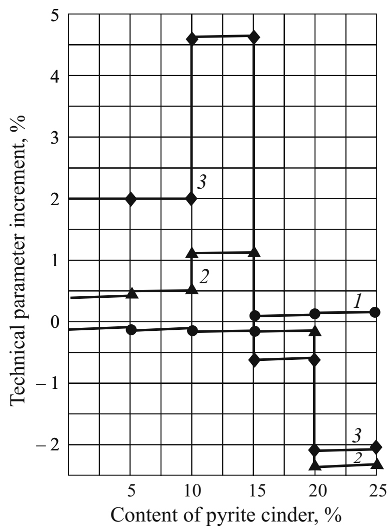

Fig. 2. Dependence of the increment rate of technical parameters on the content of pyrite cinder: *1*) water absorption; *2*) bending strength; *3*) cold resistance.

In our opinion, for a more adequate description of this phenomenon we should construct a plot of the "increment rates" of technical parameters calculated based on the formulas of numerical percentage differentiation [8]:

$$v = \frac{y(x_{i+1}) - y(x_i)}{x_{i+1} - x_i},$$

where v is the increment rate of the parameter y with increasing cinder content x on the ith segment.

Figure 2 shows the dependence of the increment rate of technical parameters on the content of pyrite cinder in roof tiles.

Assuming that the formation of new minerals ends with a level of 10% pyrite cinder in mixtures [4], it is logical to regard the next segment (10 – 15% cinder) in all plots as the segment of quantitative accumulation of positive variations. Next, after the peak at the level of 15% a new restructuring takes place with a negative dynamics of the technical parameter increment.

A content of more than 15% pyrite cinder in mixtures at the firing temperature of 1050°C does not facilitate the dissolution of cinder in ceramic mixtures (the refractoriness of cinder is 1120 – 1180°C). Apparently in this case the firing temperature of roof tiles must be raised. A ceramic mixture containing over 20% cinder has virtually no sintering interval and products molded of such mixture are prone to deformation [1, 3, 5].

Thus, the rate of the quantitative accumulation of properties (parameters) at each "stable" interval differs from the rate at the preceding segment. This is due to the decreasing content of "dangerous" pores in samples and a uniform distribution of pores of sizes $10^{-6} – 10^{-7}$ m [5].

Using differential programs (the pore content based on the radius) obtained by the mercury porosimetry method, it has been found [5] that the total volume of "dangerous'" pores (sizes $10^{-5} – 10^{-7}$ m) in samples of mixtures 1 and 3 – 5 (Table 2 and 3) formed at 1050°C is equal to (%): mixture 1) 73, 3) 83, 4) 75, and 5) 80. The most uniform distribution of pores of size $10^{-6} – 10^{-7}$ m is registered in the samples of mixture 4, where the pore content is 65%, whereas the pore content in samples 1, 3, and 5 is equal to 45, 63, and 55%. Furthermore, samples 4 contain 25% pores of size 10^{-7} m.

High physicomechanical parameters are observed in mixture 4 samples (Table 2 and 3), in which pores of size $10^{-6} – 10^{-7}$ m are distributed more uniformly [5]. Moreover, mixture 4 has the lowest content of pores of size $10^{-5} – 10^{-6}$ m, which is equal to 10%, compared to mixtures 1, 3, and 5.

Thus, the introduction of 15% pyrite cinder in ceramic mixtures significantly improves the cold resistance of roof tiles. The decrease in water absorption in this case is not proportional to the increase in cold resistance. A uniform distribution of pores of size $10^{-6} – 10^{-7}$ m significantly contributes to improving cold resistance. Furthermore, the introduction of the optimum quantity of pyrite cinder into the ceramic mixtures contributes to decreasing the content of "dangerous" pores of size $10^{-5} – 10^{-6}$ m in samples.

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